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Potential-Dependent Surface Raman Spectroscopy of Buckminsterfullerene
Films on Gold: Vibrational Characteristics of Anionic versus Neutral C₆₀

by

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ABSTRACT

Real-time surface-enhanced Raman spectra have been obtained for thin films of buckminsterfullerene (C_{60}) on gold in acetonitrile during cyclic voltammetric potential excursions. At potentials where neutral C_{60} is stable, all ten normally active Raman bands are observed, along with three weaker features that are infrared-active in the bulk-phase vibrational spectra. Upon electroreduction to the C_{60} monoanion, several Raman-active bands downshift significantly in frequency, most prominently for the A_g mode (1460 cm^{-1}), which decreases by almost 20 cm^{-1} . Additionally, several H_g bands become more intense, and in two cases yield doublets upon C_{60}^- formation, most probably reflecting a diminution in molecular symmetry.

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We report here real-time surface-enhanced Raman (SER) spectra for films of buckminsterfullerene (C_{60}) on gold in acetonitrile observed during cyclic voltammetric potential excursions. The results provide the first vibrational spectra for the C_{60} monoanion; they indicate that reduction induces significant perturbations in the bonding and symmetry characteristics of C_{60} .

Several Raman and infrared studies have been reported for neutral C_{60} ¹⁻³. Most findings are in harmony with the predicted expectation of only ten Raman-active and four infrared-active vibrations^{4,5}. Especially given this high degree of symmetry, it is of interest to examine the effects of adding an electron(s); a reduction in symmetry might be anticipated due to Jahn-Teller distortions, along with possible changes in the skeletal force constants and hence vibrational frequencies. Reversible electroreduction of solution-phase C_{60} in up to four one-electron steps occurs in suitable nonaqueous media^{3b,5,6}. The uv-visible spectroelectrochemistry of these states exhibits significant redox-induced spectral shifts⁶. The reversible electroreduction in acetonitrile of C_{60} films formed by solution evaporation on Pt, Au, or glassy carbon surfaces has recently been demonstrated⁷. Given that extended (i.e., multilayer) films as well as adsorbates on suitably roughened gold electrodes exhibit stable as well as intense SERS⁸, this observation suggests that SERS could provide a powerful means of examining the sensitivity of the C_{60} vibrational properties to the cluster oxidation state.

The gold electrode, 4 mm diameter sheathed in Teflon, was rendered SERS-active by means of the oxidation-reduction procedure described in ref. 9, and rinsed with acetonitrile prior to use. The C_{60} films were prepared by evaporating on the surface a few microliters of a ca 0.01-0.1 mM solution in dichloromethane⁷. The solid C_{60} sample was prepared and purified according to procedures in ref. 5. Acetonitrile was distilled over CaH_2 , and tetrabutylam-

monium perchlorate (TBAP) was recrystallized twice from water. An equimolar mixture of ferrocenium/ferrocene ($\text{Fc}^{+/0}$) in acetonitrile (contained in a separate compartment) was used as the reference electrode. Cyclic voltammograms run from 0 V to up to -2 V (versus $\text{Fc}^{+/0}$) for the C_{60} films in acetonitrile containing 0.1 M TBAP are similar to those reported in ref. 7. (The charge contained under the voltammetric waves provides an additional assay of the film thickness.) Sequences of SER spectra were recorded during such cyclic voltammograms by means of a SPEX Model 1877 spectrometer equipped with a Photometrics PM 512 CCD detector (see ref. 10 for other details). Laser excitation was a Kr^+ laser operated at 647 nm with ca 20 mW power on the sample. Individual spectra could be obtained every few seconds during the potential excursion, allowing the voltammetric features to be matched with the observed spectral changes¹¹.

Figures 1 and 2 show typical potential-dependent sequences of SER spectra obtained for a C_{60} film (2-3 monolayers thick) in the 240-840 cm^{-1} and 1080-1620 cm^{-1} frequency regions, respectively, every 10s during a cyclic voltammogram at 10 mV s^{-1} between 0 and -1.2 V vs $\text{Fc}^{+/0}$. (The spectra are limited to 500-600 cm^{-1} segments due to the spatial characteristics of the CCD detector at 647 nm. No significant spectral features were observed from 800-1050 cm^{-1} .) The potentials labelled alongside each spectrum are the average values during the data acquisition; the spectra are stacked so that the upward sequence refers to increasing time.

At potentials positive of ca -0.9 V, the SER spectral features are uniformly quite similar to the normal Raman bands reported for solid bulk-phase C_{60} ¹; the frequencies typically match within 5-10 cm^{-1} , and the relative intensities are comparable. A summary of these SER bands, along with the corresponding bulk-phase Raman frequencies, is given in Table I. All ten Raman-active bands anticipated from the bulk-phase selection rules (having A_g or H_g

symmetry)¹ are apparently also observed in the SER spectra. Three additional weaker bands are observed, with frequencies that match closely those reported in the bulk-phase infrared spectrum. The one remaining infrared-active band (at 1428 cm^{-1}) is accidentally degenerate with a Raman-active feature. Consequently, then, the SERS selection rules allow the normally exclusively infrared- as well as Raman-active modes of C_{60} to be observed. This symmetry lowering would appear to occur in the absence of C_{60} -surface coordination; the appearance of such Raman-forbidden bands probably reflects the influence of the surface electric field gradient.¹² The present results differ somewhat from a recent report of SERS for C_{60} on gold in aqueous media, for which a number of additional bands, attributed to distorted C_{60} species, were observed.²

The present SERS features are virtually independent of potential between 1.0 and ca -0.7 V , and of the film thickness (from ca 2–20 monolayers). Significant spectral changes, however, occur at potentials between -0.9 and -1.1 V during the forward (negative-going) sweep, which are reversed at ca -0.6 V during the return sweep (Figs. 1,2). These potentials correspond precisely to the appearance of the anodic and cathodic waves associated with the formation and reoxidation of C_{60}^- (cf ref. 7).

Several significant elements of these redox-induced spectral changes are evident, as can be seen from Figs. 1 and 2, and Table I. First, some of the Raman-active bands undergo significant (ca $5\text{--}20\text{ cm}^{-1}$) frequency downshifts upon formation of C_{60}^- from C_{60} , most prominently for the C_{60} A_g mode at 1460 cm^{-1} , which downshifts by almost 20 cm^{-1} . A comparable frequency downshift for this Raman band has been seen upon doping C_{60} with alkali metals so to yield conducting films.¹³ These effects are indicative of the weakening of C–C bonds caused by the added antibonding electron. Additionally, several bands having H_g symmetry become more intense and broader upon C_{60}^- formation; moreover, two bands (at ca

710 and 770 cm^{-1}) yield doublets (Fig. 1). These changes may well reflect a loss of the usual fivefold degeneracy of the H_g symmetry bands, arising from anticipated Jahn-Teller distortions in the monoanion.^{4b} Sweeping the potential to values negative of -1.4 V, corresponding to C_{60}^{2-} formation, yielded further frequency downshifts of the major Raman features. The bands, however, become markedly weaker and broader. Nonetheless, spectra corresponding to C_{60}^- and C_{60} reappear upon returning the potential to appropriately less negative potentials.

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TABLE I Summary of SERS band frequencies (cm^{-1}) for C_{60} and C_{60}^- , and comparison with Raman spectra for bulk-phase C_{60}

C_{60}^- ^{a,e}	C_{60} ^{b,e}	C_{60} ^{c,e}	Assignment ^d
270(s)	273(s)	273(s)	H_g squashing
420(s)	426(m)	437(m)	H_g
489(s)	492(s)	496(s)	A_g breathing
520(s)	523(w)	[527]	F_{1u}
576(w)	576(w)	[577]	F_{1u}
712(s), 700(s)	712(w)	710(w)	H_g
743(m)	743(w)		?
770(s), 760(s)	774(m)	774(m)	H_g
1100(w)	1100(w)	1099(w)	H_g
1183(w)	1183(vw)	[1183]	F_{1u}
1245(m)	1245(w)	1250(w)	H_g
1415(w)	1422(m)	1428(m), [1428]	H_g , F_{1u}
1443(s)	1461(s)	1470(vs)	A_g "pentagonal pinch"
1556(m)	1566(m)	1575(m)	H_g

^a Major SERS band frequencies for C_{60}^- , measured for C_{60} film on gold in acetonitrile at potentials between -1.0 V and -1.2 V vs $\text{Fc}^{+/0}$

^b Major SERS frequencies for C_{60} , obtained as in ^a at potentials positive of ca -0.6 V vs $\text{Fc}^{+/0}$

^c Corresponding bulk-phase Raman band frequencies for solid C_{60} , taken from ref. 1b. Values given in brackets refer to IR-active bands.

^d Vibrational band assignments, from ref. 1b

^e Band intensities: vw - very weak, w - weak, m - medium, s - strong, vs - very strong

FIGURE CAPTIONSFig. 1

Potential-dependent SER spectral sequence in $240\text{--}840\text{ cm}^{-1}$ region, obtained during 10 mV s^{-1} voltammogram from 0 to -1.2 V and return (vs Fc^+/Fc) for ca 5 monolayer C_{60} film on gold in acetonitrile containing 0.1 M TBAP. Each spectrum was acquired in 8s. The asterisked peak is due to acetonitrile. Raman excitation was at 647.1 nm , with 20 mW power; bandpass was 6 cm^{-1} .

Fig. 2

As in Fig. 1, but for $1080\text{--}1620\text{ cm}^{-1}$ region.

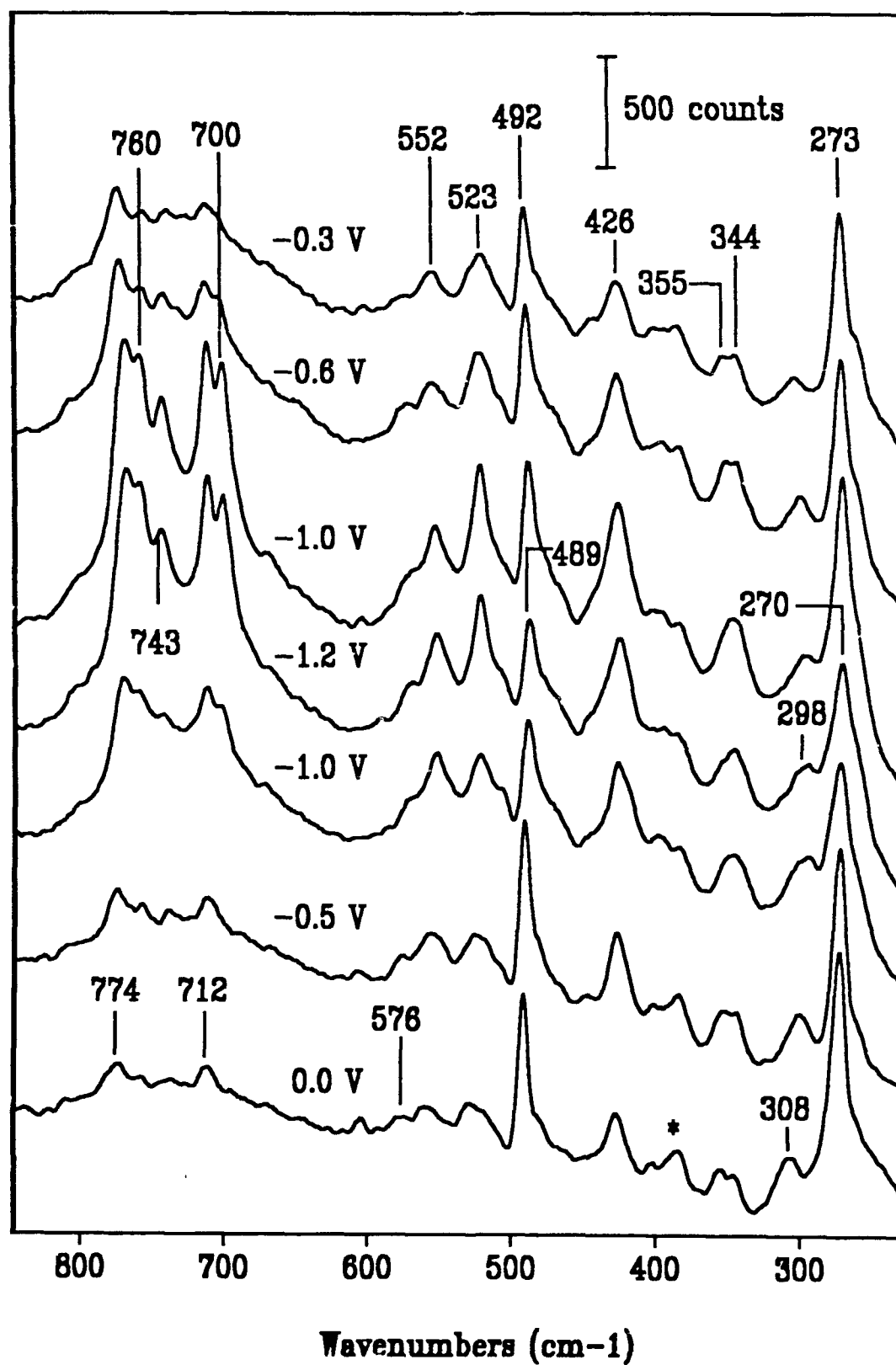


FIG 1

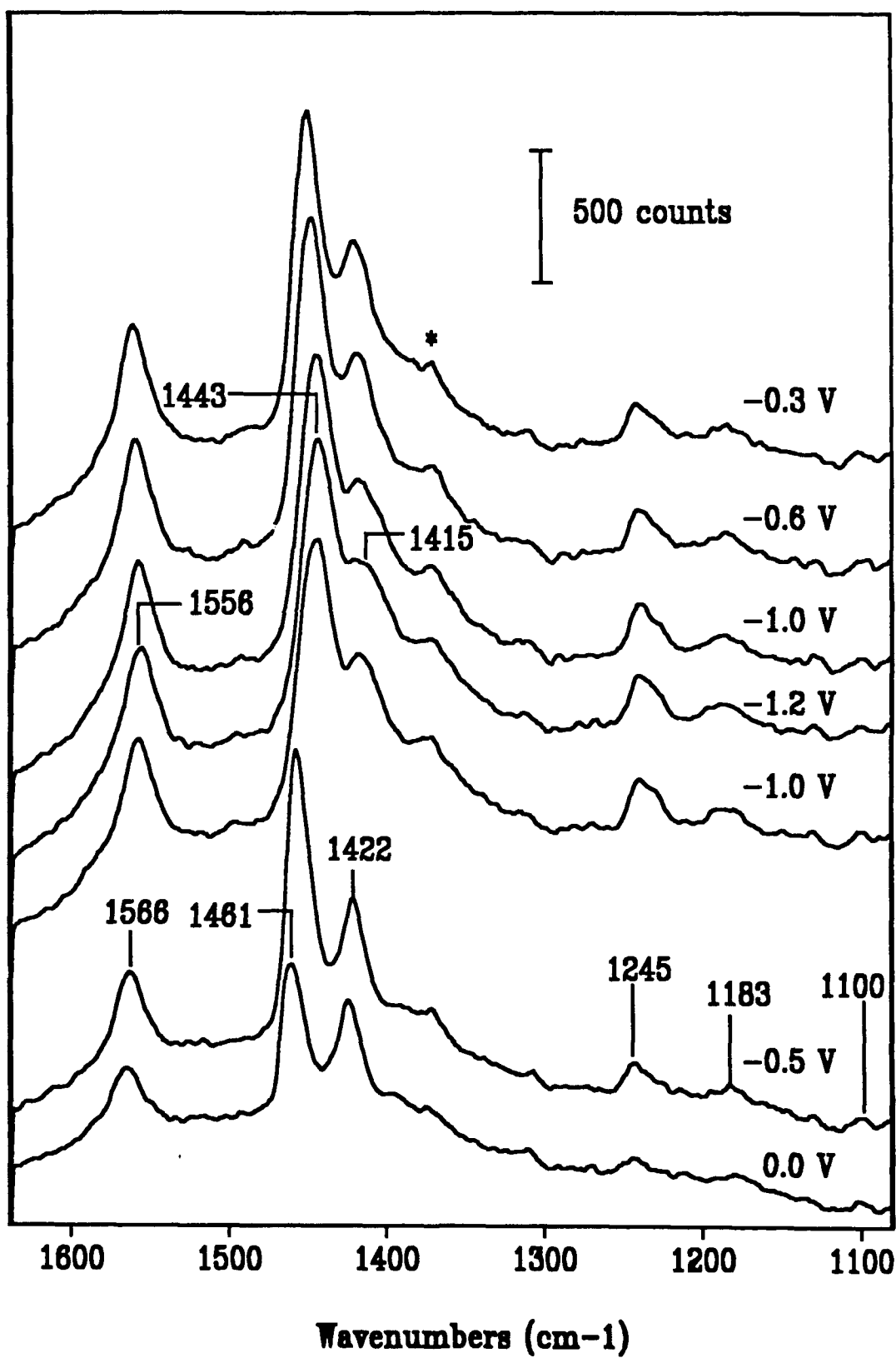


FIG 2